Description

Lubricating Oil Composition for Internal Combustion Engine

[Technical Field]

The present invention relates to lubricating oil compositions for internal combustion engines and particularly to low ash content-diesel engine oils suitable for use in diesel engines equipped with an exhaust-gas after-treatment device.

[Background Art]

With the background of world-wide environmental issues, the regulations on exhaust gas in each nation have been more strict year by year. Particularly, it is now urgently necessary to decrease the amounts of NOx and suspended particulate matters (SPM) in the exhaust gas from diesel engines. So far, it has been considered to apply some means for decreasing exhaust gas such as high-pressure blowing, exhaust gas recycling systems (EGR), oxidation catalysts, diesel particulate filters (DPF), and NOx occlusion reduction catalysts, in a diesel engine.

Among these exhaust gas-decreasing means, particularly the oxidation catalysts, NOx absorber catalysts, and DPFs used in an exhaust-gas after-treatment device are known to be shortened in

working life depending on the composition of a lubricating oil to be used. For example, in the case of using a lubricating oil containing zinc dialkyldithiophosphate (hereinafter referred to as "ZnDTP") which is known to be effective as anti-wear agents or anti-oxidants), zinc-oxides and zinc-phosphates which derived from ZnDTP during combustion accumulate on the surface of catalysts or the filter inside and thus could impair the purifying performance of an exhaust-gas after-treatment device. Therefore, it is desirous not to add ZnDTP at all in a lubricating oil for an engine equipped with an exhaust-gas after-treatment device as described above or to keep the amount of ZnDTP as minimum as possible. Similarly to ZnDTP, metal-sulfates and metal-oxides derived from metallic detergents which accumulate as ash contents and thus may cause the above-described problems.

However, due to a large amount of soot contaminating a lubricating oil in diesel engines, particularly those with equipped with an EGR, the decrease of ZnDTP and metallic detergents contents would cause the wear of valves and the deterioration of the detergency for pistons. Therefore, in order to decrease the ZnDTP and metallic detergents contents, it is necessary to study on a new means for compensating the deterioration of detergency and anti-wear

properties, resulting from the decrease of ZnDTP and metallic detergents. As lubricating oil compositions for use in diesel engines equipped with an exhaust-gas after-treatment device, Japanese Laid-Open Patent Publication No. 2000-256690 proposes diesel engine oil compositions whose sulfated ash content is decreased to 0.7 percent by mass or less.

The object of the present invention is provide low ash content-type diesel engine oils which can exhibit enhanced anti-wear properties and high temperature detergency, particularly even under the conditions where a large amount of soot contaminates the lubricant oils, suitable for use in diesel engines equipped with an exhaust-gas after-treatment device.

[Disclosures of the Invention]

As a result of an extensive research and study on a diesel engine oil capable of maintaining anti-wear properties and high temperature detergency even with the decreased amounts of ZnDTP and metallic detergents, the present invention was completed by finding that a lubricating oil composition exhibiting excellent anti-wear properties and high temperature detergency even contaminated by soot was able to be obtained by blending a specific ashless dispersant and a specific phosphorus-containing ashless anti-wear agent, alternatively with a fatty acid amide in specific amounts while decreasing the amounts of ZnDTP and

metallic detergents.

According to the present invention, there is provided an internal combustion engine lubricating oil composition which comprises a mineral and/or synthetic base oil, (A) a succinimide-based ashless dispersant in an amount of 0.08 to 0.40 percent by mass in terms of nitrogen, (B) a metallic detergent in an amount of 0.06 to 0.22 percent by mass in terms of metal element, (C) a zinc secondary alkyldithiophosphate in an amount of 0.04 to 0.08 percent by mass in terms of phosphorus, and (D) a phosphorus-containing ashless anti-wear agent in an amount of 0.01 to 0.04 percent by mass in terms of phosphorus and contains sulfated ashes derived from the metal elements in the composition in an amount of 0.3 to 1.0 percent by mass.

Furthermore, according to the present invention, there is provided an internal combustion engine lubricating oil composition which comprises a mineral and/or synthetic base oil, (A) a succinimide-based ashless dispersant in an amount of 0.08 to 0.40 percent by mass in terms of nitrogen, (B) a metallic detergent in an amount of 0.06 to 0.22 percent by mass in terms of metal element, (C) a zinc secondary alkyldithiophosphate in an amount of 0.02 to 0.08 percent by mass in terms of phosphorus, (D) a phosphorus-containing ashless anti-wear agent in an amount of 0.01 to 0.04 percent by mass in terms of

phosphorus, and (E) a fatty acid amide in an amount of 0.01 to 2.0 percent by mass and contains sulfated ashes derived from the metal elements in the composition in an amount of 0.3 to 1.0 percent by mass.

In the lubricating oil compositions of the present invention, Component (B) is preferably an alkaline earth metal salicylate. Component (D) is preferably at least one compound selected from the group consisting of phosphoric acid esters and amine salts thereof; and phosphorus acid esters and amine salts thereof. The lubricating oil compositions of the present invention are preferably used in diesel engines equipped with an exhaust-gas after-treatment device.

The present invention will be described in more details below.

No particular limitation is imposed on the lubricating base oils used in the present invention as long as they are base oils which have conventionally been used as those for lubricating oil compositions regardless of whether they are mineral base oils or synthetic ones.

Examples of such mineral base oils include those which can be obtained by subjecting a lubricating oil fraction produced by atmospheric- or vacuum-distilling a crude oil, to any one or more refining processes selected from solvent deasphalting, solvent extraction, hydrocracking, solvent dewaxing, hydrorefining, and a

wax isomerizing treatment; and those obtained by subjecting such a lubricating oil fraction to hydrocracking, hydrorefining or wax isomerizing treatment are preferably used.

Specific examples of the synthetic base oils include alkylnaphthalenes; alkylbenzenes; polybutenes and hydrides thereof; poly-α-olefins such as 1-octene oligomer and 1-decene oligomer and hydrides thereof; diesters such as ditridecyl glutarate, dioctyl adipate, diisodecyl adipate, ditridecyl adipate, and dioctyl cebacate; polyol esters such as trimethylolpropane caprylate, trimethylolpropane pelargonate, pentaerythritol-2-ethyl hexanoate, and pentaerythritol pelargonate; and mixtures thereof. Among these synthetic base oils, preferred are poly-α-olefins such as 1-octene oligomer and 1-decene oligomer and hydrides thereof.

The lubricating base oils to be used in the present invention may be any one of or combination of the above-exemplified mineral or synthetic base oils as well as mixtures of two or more of the mineral base oils or synthetic base oils. The mixing ratio of the two or more base oils can be selected arbitrary.

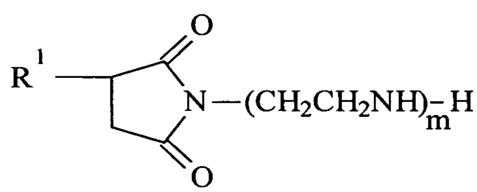
Although no particular limitation is imposed on the total aromatic content of the base oil, it is preferably 15 percent by mass or less, more preferably 13 percent by mass or less, and further more preferably

10 percent by mass or less. A lubricant base oil whose total aromatic content is more than 15 percent by mass would be poor in oxidation stability, while one whose total aromatic content is less than 2 percent by mass would not dissolve Components (A) to (D) sufficiently. Therefore, the total aromatic content is preferably 2 percent by mass or more. The term "aromatic content" used herein denotes an aromatics fraction content determined in accordance with ASTM D2549. The aromatic fraction includes alkylbenzenes, alkylnaphthalens, anthracene, phenanthrene, and alkylated products thereof, compounds wherein four or more benzene rings are condensated to each other, and compounds having heteroaromatics such as pyridines, quinolines, phenols, and naphthols.

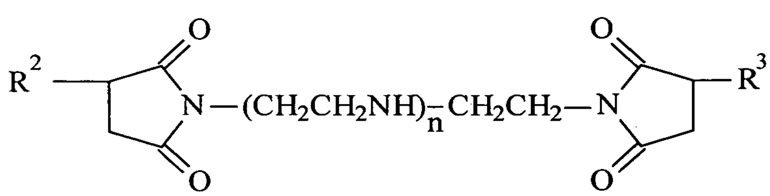
No particular limitation is imposed on the kinematic viscosity of the base oil. However, the kinematic viscosity at 100 ℃ is preferably 2 mm^2/s or higher and more preferably 3 mm^2/s or higher and is preferably 10 mm^2/s or lower and more preferably 8 mm^2/s or lower. The use of a base oil with a kinematic viscosity at 100 ℃ of 2 mm^2/s or higher is contributive to the production of a lubricating oil composition which is excellent in lubricity due to its sufficient oil film formation capability and less in evaporation loss of the base oil under high temperature conditions. Whereas, the use of a base oil with a kinematic viscosity

at 100 ℃ of 10 mm^2/s or lower makes it possible to produce a lubricating oil composition which is less in flow resistance and thus in friction resistance at the site of lubrication.

Component (A), i.e., a succinimide-based ashless dispersant of the lubricating oil composition of the present invention may be monoimides represented by formula (1) below, bisimides represented by formula (2) below, and modified products thereof with an organic acid or a boric acid:



(1)



(2)

In formulas (1) and (2), R^1, R^2, and R^3 are each independently a polybutenyl group, and m and n are each independently an integer of 2 to 5.

The polybutenyl group represented by R^1, R^2, and R^3 has a number-average molecular weight of preferably 800 or greater, more preferably 900 or greater and particularly preferably 1,500 or greater and on the other hand is preferably 3,500 or less and more preferably 2,500 or less. A polybutenyl group having a number-average molecular weight of less than 800

would decrease the detergency of the resulting lubricating oil composition. Whereas, a polybutenyl group having a number-average molecular weight of more than 3,500 would decrease the low-temperature flowability of the resulting lubricating oil composition. In order to obtain an effect of suppressing sludge formation, m and n are each independently preferably 3 or 4.

The polybutenyl group is obtained from polybutenes produced by polymerizing a mixture of 1-buten and isobutene or a highly purified isobutylene using a catalyst such as aluminum chloride- or boron fluoride-based catalysts and is preferably one in which a slight amount of chlorine and fluorine has been removed sufficiently.

No particular limitation is imposed on a method of producing the succinimide as represented by formula (1) or (2). For example, the succinimide may be produced by reacting polyamine and a polybutenyl succinimide obtained by reacting maleic anhydride and a chlorinated polybutene having a number-average molecular weight of 800 to 3,500, preferably one from which chlorine and fluorine have been sufficiently removed, at a temperature of 100 to 200 ℃. Examples of polyamine are diethylene triamine, triethylene tetramine, tetraethylene pentamine, and pentaethylene hexamine.

Examples of a method of producing a boric acid modified-succinimide are those disclosed in Japanese Patent Publication Nos. 42-8013 and 42-8014 and Japanese Laid-Open Patent Publication Nos. 51-52381 and 51-130408. More specifically, a boric acid modified-succinimide may be obtained by mixing polyamine and polybutenylsuccinic acid (anhydride) with a boron-containing compound such as boric acid, boric acid ester, or borate in a solvent including alcohols, organic solvent such as hexane or xylene, or a light fraction lubricating base oil and by heating the mixture under appropriate conditions. The boron content of the boron-modified succinimide obtained in this manner is generally from 0.1 to 4.0 percent by mass.

The lower limit content of Component (A) is 0.08 percent by mass, preferably 0.10 percent by mass, and particularly preferably 0.12 percent by mass in terms of nitrogen, based on the total mass of a composition of the present invention. The upper limit content is 0.4 percent by mass and preferably 0.3 percent by mass in terms of nitrogen, based on the total mass of the composition. Component (A) of less than 0.08 percent by mass would fail to provide the resulting composition with sufficient high-temperature detergency, while Component (A) of more than 0.4 percent by mass would deteriorate the low-temperature flowability of the resulting composition.

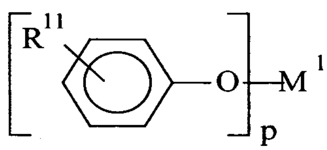
Component (B) of the internal combustion engine lubricating oil compositions of the present invention is a metallic detergent. Metallic detergents which may be used in the present invention are any of those which can be used for lubricating oils. Specific examples are one or more alkali or alkaline earth metal-based detergents selected from alkali or alkaline earth metal sulfonates, alkali or alkaline earth metal phenates, alkali or alkaline earth metal salicylates, and alkali or alkaline earth metal phosphonates.

Preferred alkali and alkaline earth metal sulfonates are alkali and alkaline earth metal salts, such as sodium, potassium, magnesium, and calcium salts, preferably magnesium and calcium salts, of alkyl aromatic sulfonic acids obtained by sulfonating alkyl aromatic compounds having a molecular weight of 300 to 1,500 and preferably 400 to 700.

Specific examples of the alkyl aromatic sulfonic acids are petroleum sulfonic acids and synthetic sulfonic acids. Petroleum sulfonic acids may be those obtained by sulfonating alkyl aromatic compounds contained in the lubricant fraction of a mineral oil or mahogany acid by-produced upon production of white oil. Synthetic sulfonic acids may be those obtained by sulfonating alkyl benzenes having a straight-chain or branched alkyl group, which may be by-produced from a plant for producing alkylbenzenes used as materials

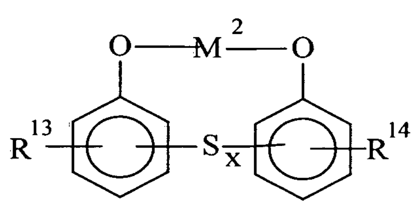
of detergents or obtained by alkylating polyolefins to benzene or those obtained by sulfonating alkylnaphtalens such as dinonylnaphthalene. Sulfonating agents used for sulfonating these alkyl aromatic compounds may be fuming sulfuric acids and sulfuric acid anhydride.

Examples of the alkali and alkaline earth metal phenates are alkali and alkaline earth metal salts, particularly sodium, potassium, magnesium, and calcium salts, of alkylphenols, alkylphenolsulfides or Mannich reaction products of alkylphenols. Specific examples are those represented by formulas (3) through (5):

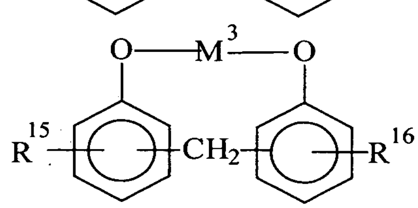


(3)

wherein R^{11} is a straight-chain or branched alkyl group having 4 to 30, preferably 6 to 18 carbon atoms, M^1 is an alkali or alkaline earth metal, p is 1 or 2, if M^1 is an alkali metal, p is 1, and if M^1 is an alkaline earth metal, p is 2;



(4)



(5)

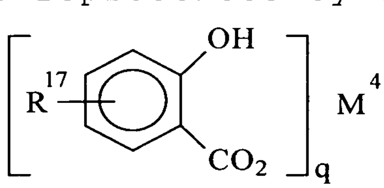
wherein R^{13}, R^{14}, R^{15}, and R^{16} are each independently a

straight-chain or branched alkyl group having 4 to 30, preferably 6 to 18 carbon atoms, M^2 and M^3 are each independently an alkaline earth metal, and x is 1 or 2.

Specific examples of the alkyl group for R^{11} and R^{13} to R^{16} are butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, heneicosyl, docosyl, tricosyl, tetracosyl, pentacosyl, hexacosyl, heptacosyl, octacosyl, nonacosyl, and triacontyl groups. These alkyl groups may be straight-chain or branched and may be of primary, secondary, or tertiary.

The above-described alkaline earth metals are preferably calcium or magnesium, and is particularly preferably calcium.

Examples of the alkali and alkaline earth metal salicylates are alkali and alkaline earth metal salts, preferably sodium, potassium, magnesium, and calcium salts, of an alkyl salicylic acid. Specific examples are compounds represented by the formula



(6)

In formula (6), R^{17} is a straight-chain or branched alkyl group having 4 to 30, preferably 6 to 18 carbon atoms, M^4 is an alkali or alkaline earth metal, q is

1 or 2, if M^4 is an alkali metal, q is 1, and if M^4 is an alkaline earth metal, q is 2.

Specific examples of the alkyl group for R^{17} are butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, heneicosyl, docosyl, tricosyl, tetracosyl, pentacosyl, hexacosyl, heptacosyl, octacosyl, nonacosyl, and triacontyl groups. These alkyl groups may be straight-chain or branched and may be of primary, secondary or tertiary.

The above-described alkaline earth metals are preferably calcium and magnesium, and is particularly preferably calcium.

The alkali or alkaline earth metal sulfonate, alkali or alkaline earth metal phenate and alkali or alkaline earth metal salicylate may be obtained by reacting an alkylaromatic sulfonic acid, an alkylphenol, an alkylphenolsuflide, a Mannich reaction product of an alkylphenol, or an alkyl salicylic acid directly with an alkali or alkaline earth metal base such as oxides or hydroxides of an alkali or alkaline earth metal.

The alkaline earth metal-based detergents are preferably used in the present invention. Other than the above-described neutral (normal salt) alkaline earth metal sulfonates, neutral alkaline earth metal

phenates and neutral alkaline earth metal salicylates, preferred detergents are basic alkaline earth metal sulfonates, basic alkaline earth metal phenates, and basic alkaline earth metal salicylates obtained by heating any of the neutral alkaline earth metal sulfonate, neutral alkaline earth metal phenate or neutral alkaline earth metal salicylate with an excess amount of an alkaline earth metal salt or alkaline earth metal base in the presence of water; and overbased alkaline earth metal sulfonates, overbased alkaline earth metal phenates, and overbased alkaline earth metal salicylates obtained by reacting a hydroxide of an alkaline earth metal with carbonic acid gas or boric acid in the presence of any of the neutral alkaline earth metal sulfonate, neutral alkaline earth metal phenate or neutral alkaline earth metal salicylate.

The above-described alkali metal salts, neutral alkaline earth metal salts, basic alkaline earth metal salts, overbased alkaline earth metal salts, and a mixture thereof may be used in the present invention. The alkali and alkaline earth metal-based detergents used in the present invention are generally those having a base number of 0 to 500 mgKOH/g. However, in order to obtain particularly excellent high-temperature detergency and anti-wear properties under conditions that the lubricating oil is deteriorated due to soot contamination, the base number

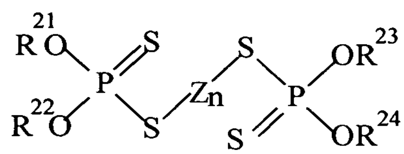
is preferably from 0 to 350 mgKOH/g and more preferably from 140 to 200 mgKOH/g. The term "base number" used herein denotes a base number measured by a perchloric acid potentiometric titration method in accordance with section 7 of JIS K2501 (1992) "Petroleum products and lubricants-Determination of neutralization number".

Although metallic detergents are usually commercially available in the form of diluted with a light lubricating base oil, it is preferable to use metallic detergents of which metal content is within the range of 1.0 to 20 percent by mass and preferably 2.0 to 16 percent by mass.

The lower limit content of Component (B) is 0.06 percent by mass, preferably 0.08 percent by mass in terms of metal element, based on the total mass of the composition. The upper limit content of Component (B) is 0.22 percent by mass, preferably 0.20 percent by mass, more preferably 0.18 percent by mass, and particularly preferably 0.14 percent by mass in terms of metal element, based on the total mass of the composition. Component (B) of less than 0.06 percent by mass would cause a difficulty in maintaining anti-wear properties, while Component (B) of more than 0.22 percent by mass would increase the amount of ash accumulating on an exhaust gas after-treatment device. In the present invention, the alkaline earth metal salicylates are

preferably used with the objective of maintaining excellent high-temperature detergency and anti-wear properties.

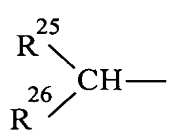
Component (C) of the internal combustion engine lubricating oil composition of the present invention is a zinc secondary alkyldithiophosphate. Specific examples of the zinc secondary alkyldithiophosphate used in the present invention are compounds represented by the formula below



(7)

In formula (7), R^{21}, R^{22}, R^{23}, and R^{24} are each independently a secondary alkyl group having 3 to 20 carbon atoms. Alkyl groups having less than 3 carbon atoms or more than 20 carbon atoms would cause a deterioration in anti-wear properties and oxidation stability of the resulting composition.

The secondary alkyl group is represented by the formula



(8)

In formula (8), R^{25} and R^{26} are each independently a straight-chain or branched alkyl group having 1 to 18 carbon atoms and the total carbon number of R^{25} and R^{26} is from 2 to 19.

Specific examples of alkyl groups for R^{25} and R^{26}

are methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, and hexadecyl groups, all of which may be of straight-chain or branched.

Preferred examples of the secondary alkyl group are isopropyl, 1-methylpropyl, and 1,3-dimethylbutyl groups, and particularly preferred is 1,3-dimethylbutyl.

One or more of the above-described zinc secondary alkyldithiophosphates may be used in the present invention.

The lower limit content of Component (C) is 0.04 percent by mass and preferably 0.05 percent by mass in terms of phosphorus based on the total mass of a composition of the present invention. The upper limit content of Component (C) is 0.08 percent by mass and preferably 0.07 percent by mass in terms of phosphorus based on the total mass of a composition of the present invention. Component (C) of less than 0.04 percent by mass would cause a difficulty in maintaining initial anti-wear properties and subsequent anti-wear properties. Component (C) of more than 0.08 percent by mass would increase the amount of ash accumulating on an exhaust-gas after-treatment device and deteriorate the high-temperature detergency.

The content of Component (C) can be decreased when used in combination with Component (E) described

hereinafter. In such a case, the lower limit content of Component (C) is 0.02 percent by mass and preferably 0.025 percent by mass in terms of phosphorus based on the total mass of a composition of the present invention. With regard to the upper content, Component (C) of even 0.08 percent by mass or less, 0.05 percent by mass or less, 0.04 percent by mass or less, or still 0.035 percent by mass or less is contributive to the production of a low ash content composition which can maintain anti-wear properties and has excellent high-temperature detergency.

Component (D) of the internal combustion engine lubricating oil composition of the present invention is a phosphorus-containing ashless anti-wear agent. Specific examples of the phosphorus-containing ashless anti-wear agent are phosphoric acid esters having a hydrocarbon group having 2 to 30, preferably 6 to 20 carbon atoms and amine salts thereof; and phosphorus acid esters having a hydrocarbon group having 2 to 30, preferably 6 to 20 carbon atoms and amine salts thereof. One or more of these compounds may be used as Component (D).

Examples of the hydrocarbon group having 2 to 30 carbon atoms are alkyl, cycloalkyl, alkylcycloalkyl, alkenyl, aryl, alkylaryl, and arylalkyl groups.

Examples of alkyl groups are ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl,

dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, and octadecyl groups, all of which may be straight-chain or branched.

Examples of cycloalkyl groups are those having 5 to 7 carbon atoms, such as cyclopentyl, cyclohexyl, and cycloheptyl groups.

Examples of alkyl cycloalkyl groups are those having 6 to 11 carbon atoms such as methylcyclopentyl, dimethylcyclopentyl, methylethylcyclopentyl, diethylcyclopentyl, methylcyclohexyl, dimethylcyclohexyl, methylethylcyclohexyl, diethylcyclohexyl, methylcycloheptyl, dimethylcycloheptyl, methylethylcycloheptyl, and diethylcycloheptyl groups, wherein the position of the alkyl group may vary.

Examples of alkenyl groups are butenyl, pentenyl, hexenyl, heptenyl, octenyl, nonenyl, decenyl, undecenyl, dodecenyl, and octadecenyl groups, which may be straight-chain or branched and the position of which double bond may vary.

Examples of aryl groups are phenyl and naphtyl groups.

Examples of alkylaryl groups are those having 7 to 12 carbon atoms, such as tolyl, xylyl, ethylphenyl, propylphenyl, butylphenyl, pentylphenyl, and hexylphenyl groups, wherein the alkyl group may be straight-chain or branched and the position thereof to

the aryl group may vary.

Examples of arylalkyl groups are those having 7 to 12 carbon atoms, such as benzyl, phenylethyl, phenylpropyl, phenylbutyl, phenylpentyl, and phenylhexyl groups, wherein the alkyl group may be straight-chain or branched.

Preferred phosphoric and phosphorus acid esters for Component (D) are monoalkyl phosphates such as monopropyl phosphate, monobutyl phosphate, monopentyl phosphate, monohexyl phosphate, monoheptyl phosphate, and monooctyl phosphate, wherein the alkyl groups may be straight-chain or branched; mono(alkyl)aryl phosphates such as monophenyl phosphate and monocresyl phosphate; dialkyl phosphates such as dipropyl phosphate, dibutyl phosphate, dipentyl phosphate, dihexyl phosphate, diheptyl phosphate, and dioctyl phosphate wherein the alkyl groups may be straight-chain or branched; di(alkyl)aryl phosphates such as diphenyl phosphate and dicresyl phosphate; trialkyl phosphates such as tripropyl phosphate, tributyl phosphate, tripentyl phosphate, trihexyl phosphate, triheptyl phosphate, and trioctyl phosphate, wherein the alkyl groups may be straight-chain or branched; tri(alkyl)aryl phosphates such as triphenyl phosphate and tricresyl phosphate; monoalkyl phosphites such as monoproyl phosphite, monobutyl phosphite, monopentyl phosphite, monohexyl phosphite,

monoheptyl phosphite, and monooctyl phosphite, wherein the alkyl groups may be straight-chain or branched; mono(alkyl)aryl phophites such as monophenyl phosphite and monocresyl phosphite; dialkyl phosphites such as dipropyl phosphite, dibutyl phosphite, dipentyl phosphite, dihexyl phosphite, diheptyl phosphite, and dioctyl phosphite, wherein the alkyl groups may be straight-chain or branched; di(alkyl)aryl phosphites such as diphenyl phosphite and dicresyl phosphite; trialkyl phosphites such as tripropyl phosphite, tributyl phosphite, tripentyl phosphite, trihexyl phosphite, triheptyl phosphite, and trioctyl phosphite, wherein the alkyl groups may be straight-chain or branched; tri(alkyl)aryl phosphites such as triphenyl phosphite and tricresyl phosphite; and mixtures thereof.

Specific examples of the amine salts of phosphoric- or phosphorus- acid esters are those obtained by allowing monophosphate, diphosphate, monophosphite, or diphosphite, to react with a nitrogen-containing compound such as ammonia or an amine compound having in its molecules only hydrocarbon or hydroxyl-containing hydrocarbon groups having 1 to 20 carbon atoms so as to neutralize the whole or part of the remaining acid hydrogen.

Specific examples of the nitrogen-containing compound are ammonia; alkyl or alkenyl amines, of which

the alkyl or alkenyl group may be straight-chain or branched, such as monomethylamine, monoethylamine, monopropylamine, monobutylamine, monopentylamine, monohexylamine, monoheptylamine, monooctylamine, monostearylamine, monooleylamine, monopropenylamine, monobutenylamine, monooctenylamine, monooctadecenylamine, dimethylamine, methylethylamine, diethylamine, methylpropylamine, ethylpropylamine, dipropylamine, methylbutylamine, ethylbutylamine, propylbutylamine, dibutylamine, dipentylamine, dihexylamine, diheptylamine and dioctylamine; alkanolamines, of which the alkanol group may be straight-chain or branched, such as monomethanolamine, monoethanolamine, monopropanolamine, monobutanolamine, monopentanolamine, monohexanolamine, monoheptanolamine, monooctanolamine, monononanolamine, dimethanolamine, methanolethanolamine, diethanolamine, methanolpropanolamine, ethanolpropanolamine, dipropanolamine, methanolbutanolamine, ethanolbutanolamine, propanolbutanolamine, dibutanolamine, dipentanolamine, dihexanolamine, diheptanolamine and dioctanolamine; and mixtures thereof.

In the present invention, triphenylphosphite and oleylamine salts of stearylhydrogen phosphite are

preferably used because they can maintain excellent anti-wear properties and high-temperature detergency.

One or more of these Components (D) may be used in the present invention. The lower limit content of Component (D) is 0.01 percent by mass and preferably 0.015 percent by mass in terms of phosphorus based on the total mass of a lubricating oil composition of the present invention, while the upper limit content is 0.04 percent by mass and preferably 0.035 percent by mass in terms of phosphorus based on the total mass of a lubricating oil composition of the present invention. Component (D) of less than 0.01 percent by mass would cause a difficulty in maintaining initial anti-wear properties and subsequent anti-wear properties, while Component (D) of more than 0.04 percent by mass would extremely deteriorate the oxidation stability of the resulting lubricating oil composition.

Component (E) of the internal combustion engine lubricating oil composition of the present invention is a fatty acid amide. Although the fatty acid of the fatty acid amide may be straight-chain or branched and saturated or unsaturated fatty acids, the alkyl group or alkenyl group thereof has 6 to 30, preferably 9 to 24, and more preferably 12 to 20 carbon atoms. Fatty acids having an alkyl or alkenyl group of fewer than 6 carbon atoms would deteriorate the solubility of Component (E), while those having an alkyl or alkenyl

group of more than 30 carbon atoms would deteriorate the anti-wear properties.

Specific examples of the fatty acid are straight-chain or branched saturated fatty acids, such as heptanoic acid, octanonic acid, nonanoic acid, decanoic acid, undecanoic acid, dodecanoic acid, tridecanoic acid, tetradecanoic acid, pentadecanoic acid, hexadecanoic acid, heptadecanoic acid, octadecanoic acid, nonadecanoic acid, eicosanoic acid, heneicosanoic acid, docosanoic acid, tricosanoic acid, tetracosanoic acid, pentacosanoic acid, hexacosanoic acid, heptacosanoic acid, octacosanoic acid, nonacosanoic acid, and triacontanoic acid; and straight-chain or branched unsaturated fatty acids, the position of which double bond may vary, such as heptenoic acid, octenoic acid, nonenoic acid, decenoic acid, undecenoic acid, dodecenoic acid, tridecenoic acid, tetradecenoic acid, pentadecenoic acid, hexadecenoic acid, heptadecenoic acid, octadecenoic acid, nonadecenoic acid, eicosenoic acid, heneicosenoic acid, docosenoic acid, tricosenoic acid, tetracosenoic acid, pentacosenoic acid, hexacosenoic acid, heptacosenoic acid, octacosenoic acid, nonacosenoic acid, and triacontenoic acid.

Specific examples of the fatty acid amide for Component (E) are amides obtained by reacting any of the above-exemplified fatty acids or acid chlorides

thereof with a nitrogen-containing compound such as ammonia and amine compounds having in per molecule only hydrocarbon or hydroxyl-containing hydrocarbon groups having 1 to 20 carbon atoms.

Specific examples of the nitrogen-containing compound are ammonia; alkylamine, of which the alkyl group may be straight-chain or branched, such as monomethylamine, monoethylamine, monopropylamine, monobutylamine, monopentylamine, monohexylamine, monoheptylamine, monooctylamine, dimethylamine, methylethylamine, diethylamine, methylpropylamine, ethylpropylamine, dipropylamine, methylbutylamine, ethylbutylamine, propylbutylamine, dibutylamine, dipentylamine, dihexylamine, diheptylamine and dioctylamine; alkanolamines, of which the alkanol group may be straight-chain or branched, such as monomethanolamine, monoethanolamine, monopropanolamine, monobutanolamine, monopentanolamine, monohexanolamine, monoheptanolamine, monooctanolamine, monononanolamine, dimethanolamine, methanolethanolamine, diethanolamine, methanolpropanolamine, ethanolpropanolamine, dipropanolamine, methanolbutanolamine, ethanolbutanolamine, propanolbutanolamine, dibutanolamine, dipentanolamine, dihexanolamine, diheptanolamine, and dioctanolamine; and mixtures

thereof.

In the present invention, stearic acid amide and oleic acid amide are preferably used because of their excellent initial anti-wear properties and a capability of maintaining anti-wear properties.

The use of Component (E) in the internal combustion engine lubricating oil composition of the present invention can decrease the content of Component (C). The lower content of Component (E) is 0.01 percent by mass and preferably 0.05 percent by mass based on the total mass of a composition of the present invention, while the upper limit content is 2.0 percent by mass and preferably 1.0 percent by mass based on the total mass of a composition of the present invention. Component (E) of less than 0.01 percent by mass would cause a difficulty in maintaining anti-wear properties, while Component (E) of more than 2.0 percent by mass would deteriorate the storage stability of the resulting composition.

The internal combustion engine lubricating oil composition of the present invention contains sulfated ash derived from the metal elements in an amount of 0.3 to 1.0 percent by mass. The lower limit sulfated ash content is preferably 0.4 percent by mass, more preferably 0.45 percent by mass, and further more preferably 0.50 percent by mass. The upper limit sulfated ash content is preferably 0.8 percent by mass,

more preferably 0.65 percent by mass, and particularly preferably 0.6 percent by mass. A sulfated ash content of less than 0.3 percent by mass would cause a difficulty in maintaining anti-wear properties as mentioned above, while a sulfated ash content of more than 1.0 percent by mass would exert undesired influences such as the accumulation of ash on an exhaust gas after-treatment device and the occurrence of clogging caused by ash particularly in a DPF.

If necessary, various additives such as ashless dispersants other than Component (A), anti-wear agents other than Components (C) and (D), friction modifiers other than Component (E), oxidation inhibitors, rust preventives, anti-emulsifiers, metal deactivators, and antifoamer may be added to the lubricating oil composition of the present invention to an extent that the achievement of the purpose of the invention is not bothered.

Examples of ashless dispersants other than Component (A) are benzylamines having in per molecule at least one alkyl or alkenyl group having 40 to 400 carbon atoms and derivatives thereof; and polyamines having in per molecule at least one alkyl or alkenyl group having 40 to 400 carbon atoms and derivatives thereof.

Examples of friction modifiers other than Components (C) and (D) are sulfur-based compounds such

as thiophosphates having in per molecule 1 to 4 sulfur atoms, thiophosphites having in per molecule 1 to 3 sulfur atoms, amine salts thereof, disulfides, olefin sulfides, dithiocarbamates, and sulfurized fats and oils. Although zinc primary dialkyldithiophosphates and zinc diaryldithiophosphates may be added, the lubricating oil composition of the present invention preferably contains only zinc dithiophosphates as defined with respect to Component (C).

Friction modifiers other than Component (E) are molybdenum dithiocarbamate, molybdenum dithiophosphate, fatty acid esters having a hydrocarbon group of 6 to 30 carbon atoms, and aliphatic amines.

Examples of oxidation inhibitors are various phenol-, amine-, and sulfur-based compounds.

Examples of rust preventives are alkenyl succinic acid esters and polyhydric alcohol esters.

Examples of anti-emulsifiers are polyalkylene glycol-based non-ionic surfactants such as polyoxyethylenealkyl ether, polyoxyethylenealkylphenyl ether, and polyoxyethylenealkylnaphthyl ether.

Examples of metal diactivators are benzotriazole-, benzimidazole-, benzothiazole-, and thiadiazole-based compounds.

Examples of antifoamers are dimethylpolysiloxane

and polyacrylates.

The internal combustion engine lubricating oil composition of the present invention contains ashless dispersants other than Component (A), anti-wear agents other than Components (C) and (D), friction modifiers other than Component (E), oxidation inhibitors, rust preventives, and anti-emulsifiers in an amount of 0.01 to 5 percent by mass, respectively, metal deactivators in amount of 0.005 to 1 percent by mass, antifoamers in an amount of 0.0005 to 1 percent by mass, based on the total mass of the composition.

[Best Modes for Carrying out the Invention]

Hereinafter, the present invention will be described in more details by way of the following examples and comparative examples, which should not be construed as limiting the scope of the invention.

[Examples 1 to 7 and Comparative Examples 1 to 6]

Various lubricating oil compositions were prepared in accordance with the formulations shown in Tables 1 (Examples 1 to 7) and 2 (Comparative Examples 1 to 6) and evaluated by the following performance evaluation tests. Tables 1 and 2 also show the results of these tests.

(1) High-velocity four-ball test

1) Using fresh lubricating oil compositions

3 percent by mass of carbon black was blended with each of the lubricating oil compositions and stirred

by a homogenizer at a rotation speed of 25,000 rpm for 10 minutes. Each of the test oils was subjected to a test in accordance with ASTM D417-82 (Shell high-velocity four-ball wear test) at a temperature of 80 ℃, rotation speed of 1,800 rpm, and load of 30 kg for 30 minutes to measure the wear scar diameter.

(2) Using lubricating oil compositions after deterioration

After each of the compositions was forced to deteriorate at a temperature of 165.5 ℃ for 24 hours in accordance with "Lubricating Oils for Internal Combustion Engine-Determination of Oxidation Stability Test" (Indiana Stirring Oxidation Test (ISOT), JIS K 2514), 3 percent by mass of carbon black was blended with each of the deteriorated oil compositions thereby preparing deteriorated test oils. The same wear test as described above was conducted on the deteriorated test oils to measure the wear scar diameter.

(2) Hot tube test

The high-temperature detergency of each of the lubricating oil compositions was evaluated using a hot tube tester HT-201 manufactured by Komatsu Engineering (K.K.). In this test, each of the sample compositions was continuously fed at a flow rate of 0.3 ml/hr with an air of a flow rate of 10 ml/minute for 16 hours through a soft glass tube heated at a temperature of 290 ℃ by

a pure aluminum igniting block. After the glass tube was washed with petroleum ether, the high-temperature detergency was evaluated from the deposit produced on the inner surface of the tube on the basis of 10 points. A rating of 10 indicates a transparent and colorless inner surface (no deposit), while a rating of 0 indicates a black and opaque surface. A glass tube with the inner surface within the range of 0 to 10 was evaluated by 0.5 with reference standard tubes having been produced per rating. At a temperature of 290 ℃, a lubricating oil with a rating of 6 or higher is considered as one excellent in detergency.

Table 1

	Examples						
	1	2	3	4	5	6	7
Base Oil / Mineral Oil 1)	balance	balance	balance	balance	balance	balance	balance
(A) Succinimide-bassed ashless dispersant 2)	8.0	8.0	8.0	8.0	8.0	8.0	8.0
(N concentration: mass%)	0.13	0.13	0.13	0.13	0.13	0.13	0.13
(B) Mettalic detergents							
Ca salicylate 3)	2.0			2.0	2.0	2.0	2.0
Ca sulfonate 4)		0.8					
Ca phenate 5)			1.2				
(C) Zinc sec-alkyldithiophosphate 6)	0.95	0.95	0.95	0.95	0.95	0.70	0.40
(P concentration: mass%)	0.068	0.068	0.068	0.068	0.068	0.050	0.029
(D) Phosphorus-containing ashless wear inhibitor							
Phosphite 7)				0.8			
Amine salt of phosphite 8)	1.0	1.0	1.0			0.6	0.5
Acid phosphate 9)					0.5		
(P concentration: mass%)	0.025	0.025	0.025	0.024	0.031	0.015	0.013
(E) Fatty acid amide 10)							0.3
Other additives 11)	2.6	2.6	2.6	2.6	2.6	2.6	2.6
Ca concentration: mass%	0.12	0.10	0.11	0.12	0.12	0.12	0.12
Zn concentration: mass%	0.074	0.074	0.074	0.074	0.074	0.055	0.031
P concentration: mass%	0.093	0.093	0.093	0.092	0.099	0.065	0.041
N concentration: mass%	0.18	0.18	0.18	0.17	0.17	0.18	0.17
Sulfated ash content: mass%	0.62	0.57	0.61	0.62	0.62	0.59	0.56
(1) High-velocity four-ball wear test							
Wear scar diameter (Flesh oil): mm	0.35	0.35	0.36	0.36	0.35	0.35	0.36
Wear scar diameter (Oil deteriorated by ISOT): mm	0.36	0.40	0.41	0.36	0.40	0.35	0.40
(2) Hot tube test							
Rating (290℃,16h)	7.5	7.0	7.0	7.0	7.0	7.5	8.0

Table 2

	Comparative Examples					
	1	2	3	4	5	6
Base Oil / Mineral Oil 1)	balance	balance	balance	balance	balance	balance
(A) Succinimide-bassed ashless dispersant 2)	8.0	8.0	3.0	8.0	8.0	8.0
(N concentration: mass%)	0.13	0.13	0.05	0.13	0.13	0.13
(B) Mettalic detergents						
Ca salicylate 3)	0.7		2.0	2.0	2.0	2.0
Ca sulfonate 4)		0.3				
Ca phenate 5)						
(C) Zinc sec-alkyldithiophosphate 6)	0.95	0.95	0.95	0.95		0.4
(P concentration: mass%)	0.068	0.068	0.068	0.068	0.000	0.029
(D) Phosphorus-containing ashless wear inhibitor						
Phosphite 7)						
Amine salt of phosphite 8)	1.0	1.0	1.0		1.0	0.5
Acid phosphate 9)						
(P concentration: mass%)	0.025	0.025	0.025	0.0	0.025	0.013
(E) Fatty acid amide 10)						
Other additives 11)	2.6	2.6	2.6	2.6	2.6	2.6
Ca concentration: mass%	0.04	0.04	0.12	0.12	0.12	0.12
Zn concentration: mass%	0.074	0.074	0.074	0.074	0.0	0.031
P concentration: mass%	0.093	0.093	0.093	0.068	0.025	0.041
N concentration: mass%	0.18	0.18	0.10	0.17	0.18	0.17
Sulfated ash content: mass%	0.37	0.36	0.62	0.62	0.49	0.55
(1) High-velocity four-ball wear test						
Wear scar diameter (Flesh oil): mm	0.34	0.34	0.34	0.71	0.67	0.66
Wear scar diameter (Oil deteriorated by ISOT): mm	0.70	0.70	0.39	0.79	0.75	0.69
(2) Hot tube test						
Rating (290°C,16h)	7.5	7.5	2.5	7.0	7.0	8.0

1) to 11) in Tables 1 and 2 are as follows:

1) Hydrorefined mineral oil (kinematic viscosity: 4 mm^2/s (@100℃), viscosity index: 120)

2) Borated bis-polybutenyl succinimide (bis-type, the number-average molecular weight of polybutenyl : 1,300, nitrogen content: 1.6 mass%, boron content: 0.5 mass%)

3) Calcium carbonate-containing overbased calcium salicylate

(base number: 166, calcium content: 5.8 mass%, sulfated ash content: 19.7 mass%)

4) Calcium carbonate-containing overbased calcium sulfonate
(base number: 320, calcium content: 12.5 mass%, sulfated ash content: 42.5 mass%)

5) Calcium carbonate-containing overbased calcium phenate
(base number: 250, calcium content: 9.25 mass%, sulfated ash content: 31.5 mass%)

6) Zinc dialkyldithiophosphate
(zinc content: 7.8 mass%, phosphorus content: 7.2 mass%, alkyl group: 1,3-dimethylbutyl group)

7) Triphenylphosphite (phosphorus content: 3.0 mass %)

8) Oleyl amine salt of stearyl hydrogen phosphite (phosphorus content: 2.5 mass%, nitrogen content: 0.35 mass%)

9) Isostearyl acid phosphate (phosphorus content: 6.2 mass%)

10) Oleamide (iodine value: 80-90)

11) Phenol-based oxidation inhibitor, amine-based oxidation inhibitor, and polymethacrylate-type viscosity index improver

As apparent from the results shown in Tables 1 and 2, although the internal combustion engine lubricating oil compositions of the present invention (Examples 1 to 7) were low in ash content, they exhibited excellent anti-wear properties and high-temperature detergency. Particularly, they were highly efficient in anti-wear properties that even after they were deteriorated, and they could maintain almost the same anti-wear properties as they were fresh.

Whereas, the compositions of Comparative Examples 1 and 2 containing Component (B) in an amount too less than that defined in the present invention were decreased in anti-wear properties after deterioration. The composition of Comparative Example 3 containing Component (A) in an amount too less than that defined in the present invention failed to obtain sufficient high-temperature detergency. The compositions of Comparative Examples 4 and 5 containing no Component (D) or (C) and of Comparative Example 6 containing Component (C) in an amount too less than that defined in the present invention failed to obtain sufficient anti-wear properties.

[Applicability in the Industry]

The internal combustion engine lubricating oil compositions of the present invention though containing a small amount of ash are excellent in anti-wear properties and high-temperature detergency

and particularly exhibit excellent anti-wear properties when they are fresh and even after they are deteriorated due to the contamination of soot. Therefore, the lubricating oil compositions of the present invention are preferably used for diesel engines equipped with an exhaust-gas after-treatment device such as an EGR, an oxidation catalyst, a NOx occlusion reduction catalyst, or a DPF and can be used as lubricating oils for diesel engines for electric generator and vessels, gas engines, and gasoline engines for two- or four-wheel vehicles.